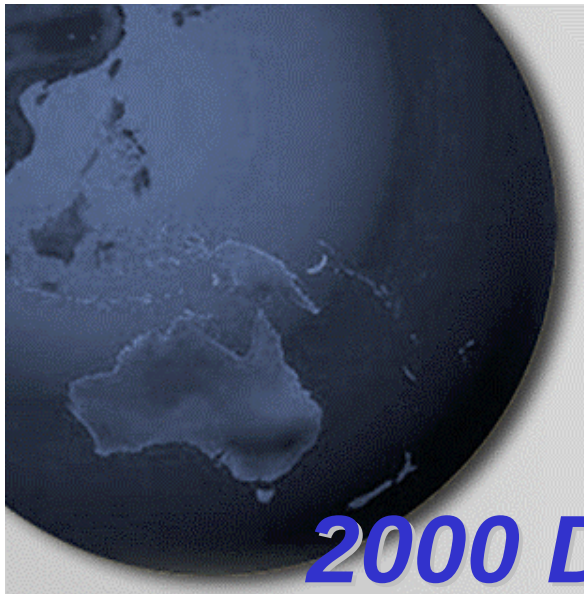


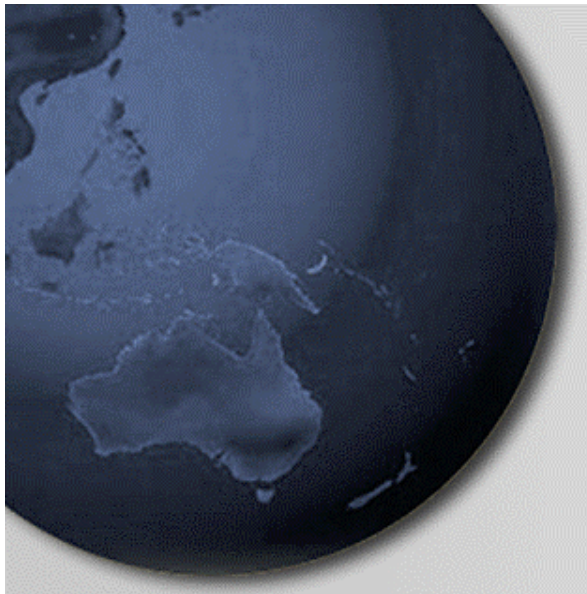
2000 DOE/SURE Presentation
Aerosol Mass Spectrometer

Cynthia A. Randles

Mentors: Dr. John Jayne and Douglas Worsnop
Aerodyne Research, Inc.

Dr. Paul Davidovits, Boston College

Jim Morris, Boston College



Aerodyne Research, Inc
Center for Aerosol and Cloud Chemistry

The Center for Aerosol and Cloud Chemistry at ARI performs laboratory and field experiments to understand heterogeneous processes associated with aerosol and cloud particles in the atmosphere. This includes processes that both directly determine the distribution of both size and chemical composition of aerosols as well as gas-particle interactions that impact gas phase species. Extensive laboratory studies have investigated the fundamental kinetics and thermodynamics of gas/liquid interactions. Current programs are developing advanced field measurement techniques for sampling ambient atmospheric particles from ground based and airborne platforms. Research and development activities are supported by government agencies, private companies and private sector research consortia. Government sponsors include: the National Science Foundation, the National Aeronautics and Space Administration, the Department of Energy, the Environmental Protection Agency, and the Office of Naval Research. Private sector sponsors include: the Electric Power Research Institute, the Coordinating Research Council, Air Products, Inc,. the Alternative Fluorocarbon Environmental Acceptability Study and the Chemical Manufacturers Association.

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Abstract

Atmospheric aerosols affect climatic change and human health. Recently, this fact has fueled the need for instrumentation that can provide real-time analysis of the size, mass and chemical composition of aerosols in both the field and laboratory. The Aerosol Mass Spectrometer (AMS) developed by Aerodyne Research, Inc. combines an innovative aerodynamic aerosol inlet developed at the University of Minnesota with standard vacuum and mass spectrometric technologies to achieve this goal. The inlet focuses particles into a narrow beam and transports them efficiently into a vacuum where their aerodynamic particle size can be determined with a particle time-of-flight (TOF) measurement. Then, time-resolved particle mass detection is performed with a quadrupole mass spectrometer after flash vaporization on a resistively heated surface (Jayne *et. al*., 1999).

In order to test the efficiency of the AMS, its results must be compared to those of more established technologies. A constant output atomizer was used to produce aerosols. Particles of a certain size were then selected using a differential mobility analyzer (DMA). The output from the DMA was then fed to both a condensation particle counter (CPC) and the AMS, and the results were compared. NH_4NO_3, DOP, and oleic acid aerosols were studied in this manner.

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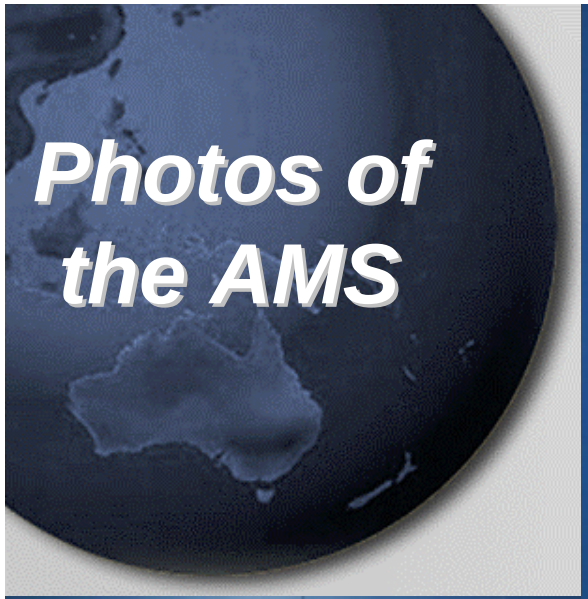
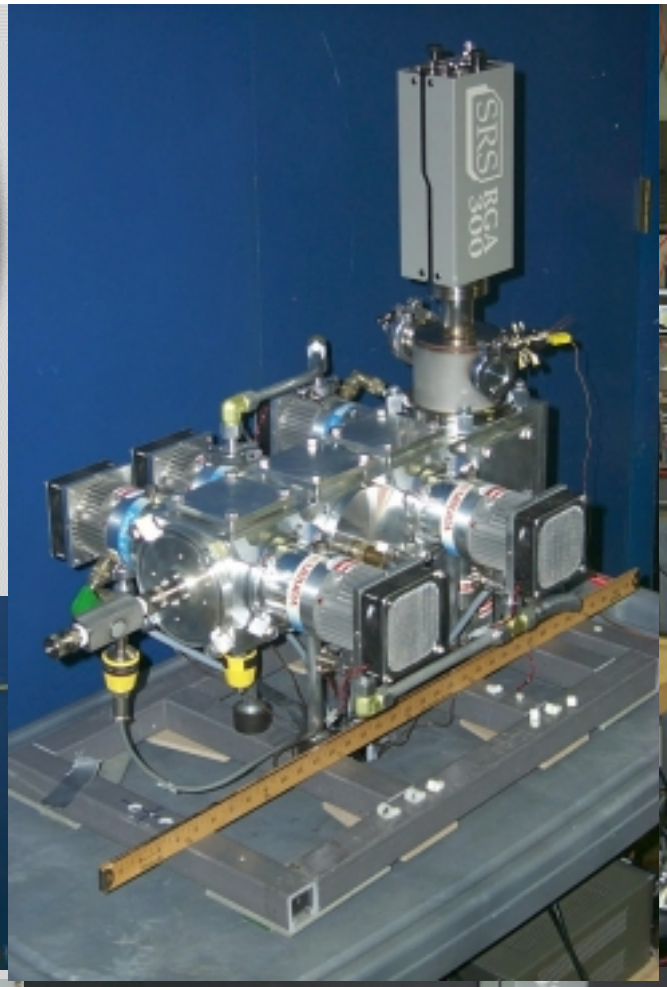
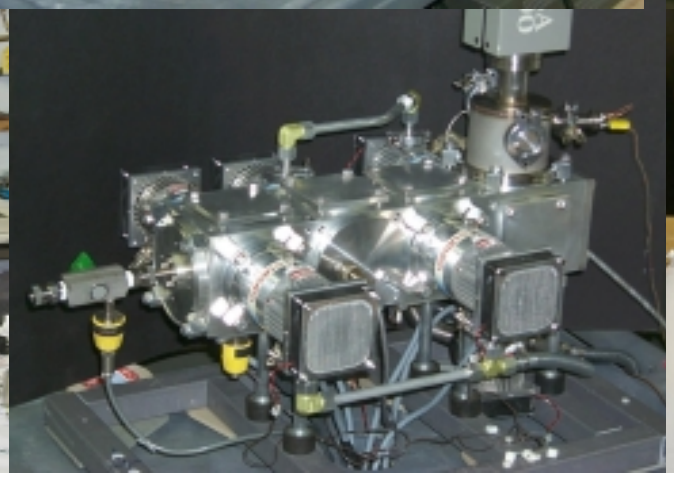
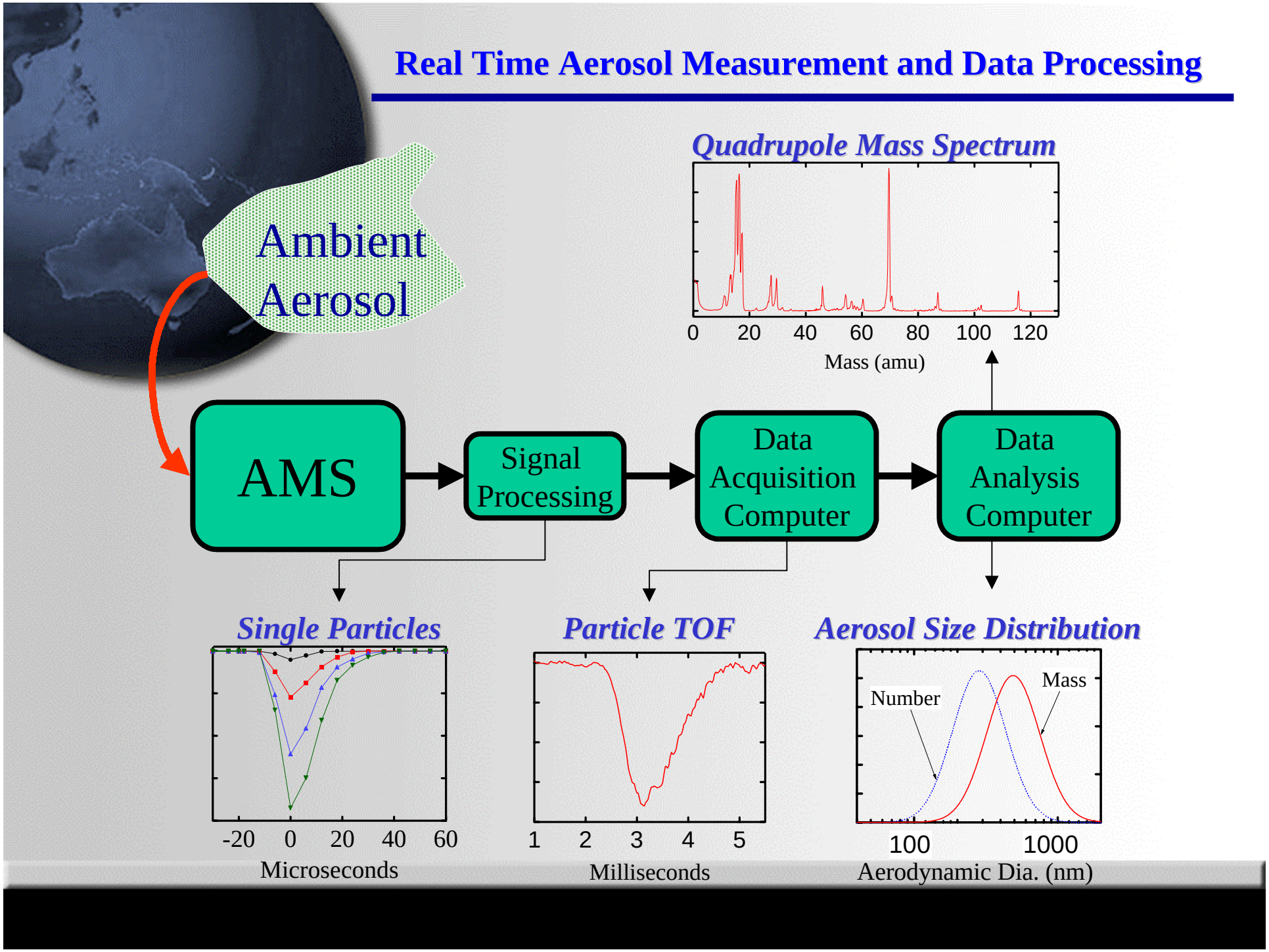
Photos of the AMS







Real Time Aerosol Measurement and Data Processing



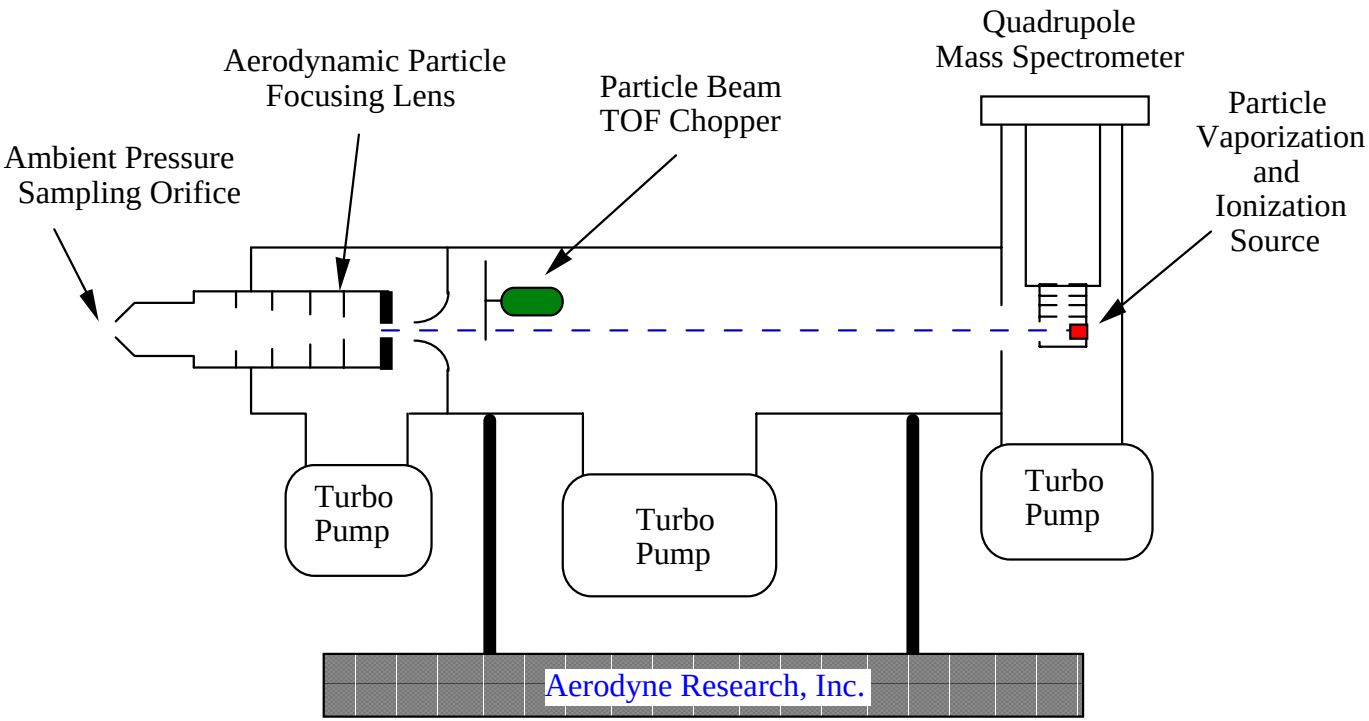
AMS Schematic

Aerosol Mass Spectrometer for Real-Time Size and Composition Analysis of Submicron Particles

Particle Beam Generation

Aerodynamic Sizing

Particle Composition

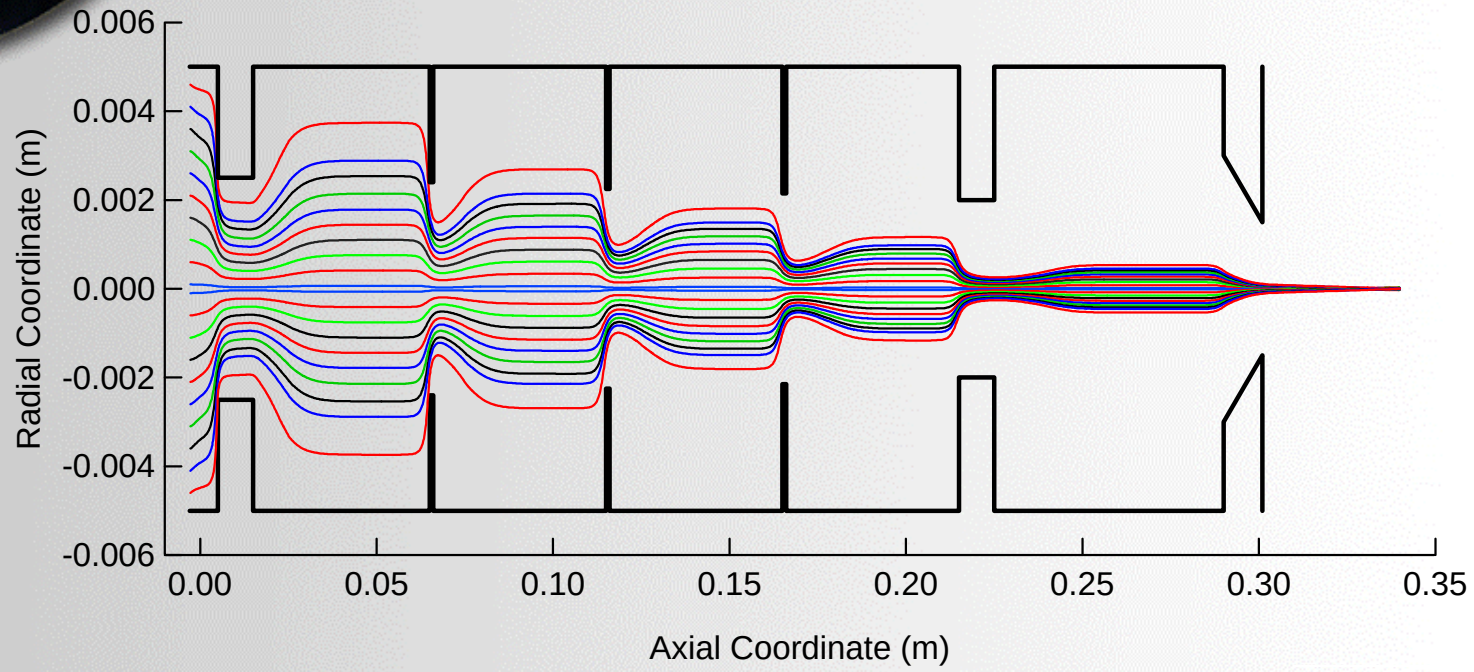


Aerosol Sampling Chamber

- The aerosol sampling chamber (ASC) couples the aerodynamic particle beam-forming lens to the vacuum system.
- The lens tube consists of six precision machined orifice lenses ranging from 5 mm inner diameter at the entrance to 3 mm inner diameter at the exit.
- The lens focuses particles into a narrow beam (~1 mm diameter) with nearly 100% particle transmission efficiency to the detector for particles with diameters between 70 and 500 nm.

Lens Transmission Efficiency

Calculated Particle Trajectories in Aerodynamic Lens
100 nm Diameter Unit Density Spheres
(Fluent ver 4.47)



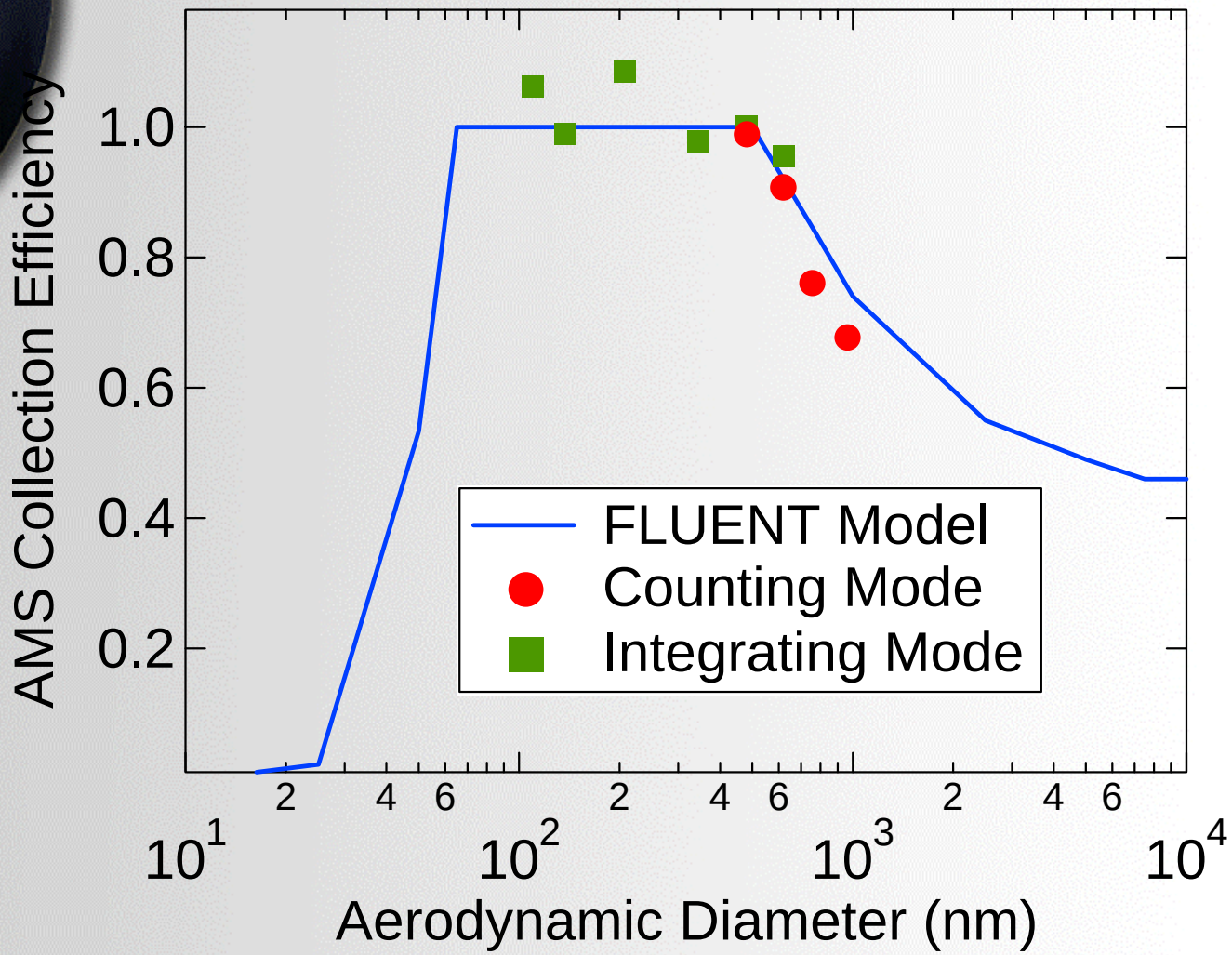
2.4 torr Inlet

10^{-3} torr Exit

Collection Efficiency

Measured Particle Collection Efficiencies Compared to FUENT Model Prediction NH_4NO_3

- 100% for 70 nm to 500 nm diameter particles.
- Particle collection drops off for small sizes due to reduced focusing efficiency
- Collection decreases for larger particles due to impaction losses at lens entrance.



Particle-Sizing Chamber

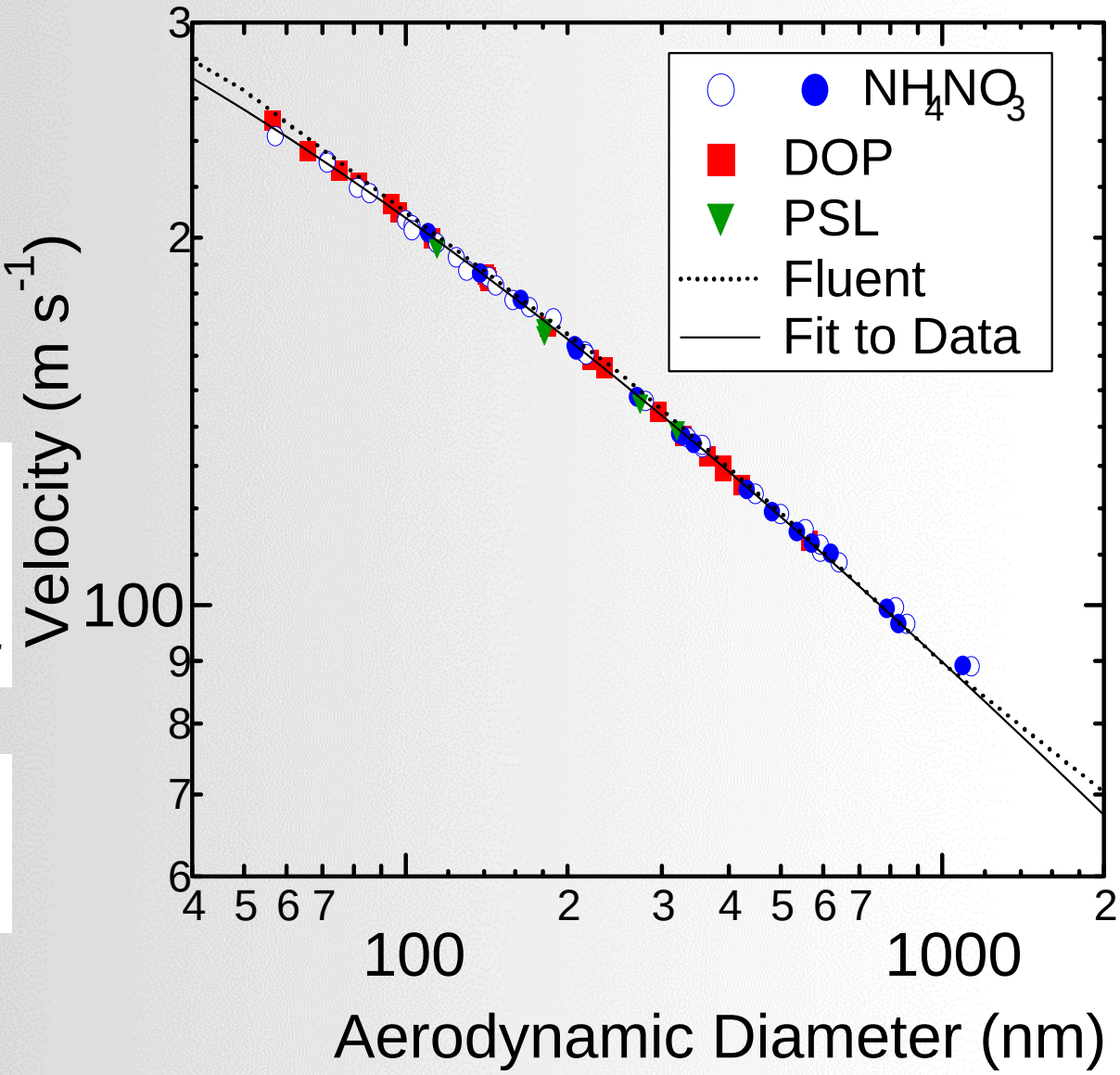
- The final orifice of the lens controls the supersonic gas expansion and particle acceleration into the particle-sizing chamber (PSC):
  - During the gas expansion, smaller diameter particles accelerate to faster velocities than larger ones due to different inertias; thus, a distribution of velocities is obtained.
  - The particle beam enters the vacuum-pumped PSC, and the beam is chopped by a 5 cm diameter wheel with two radial slits 180 degrees apart; an infrared photo-diode detector monitors the slit that the beam passes through and defines the start of the Time of Flight (TOF) measurement.
  - Using the chopper and the detection time, the TOF can be determined. Coupled with a known flight distance, the particles velocity and thus aerodynamic diameter can be obtained.

Velocity-Aerodynamic Diameter Calibration

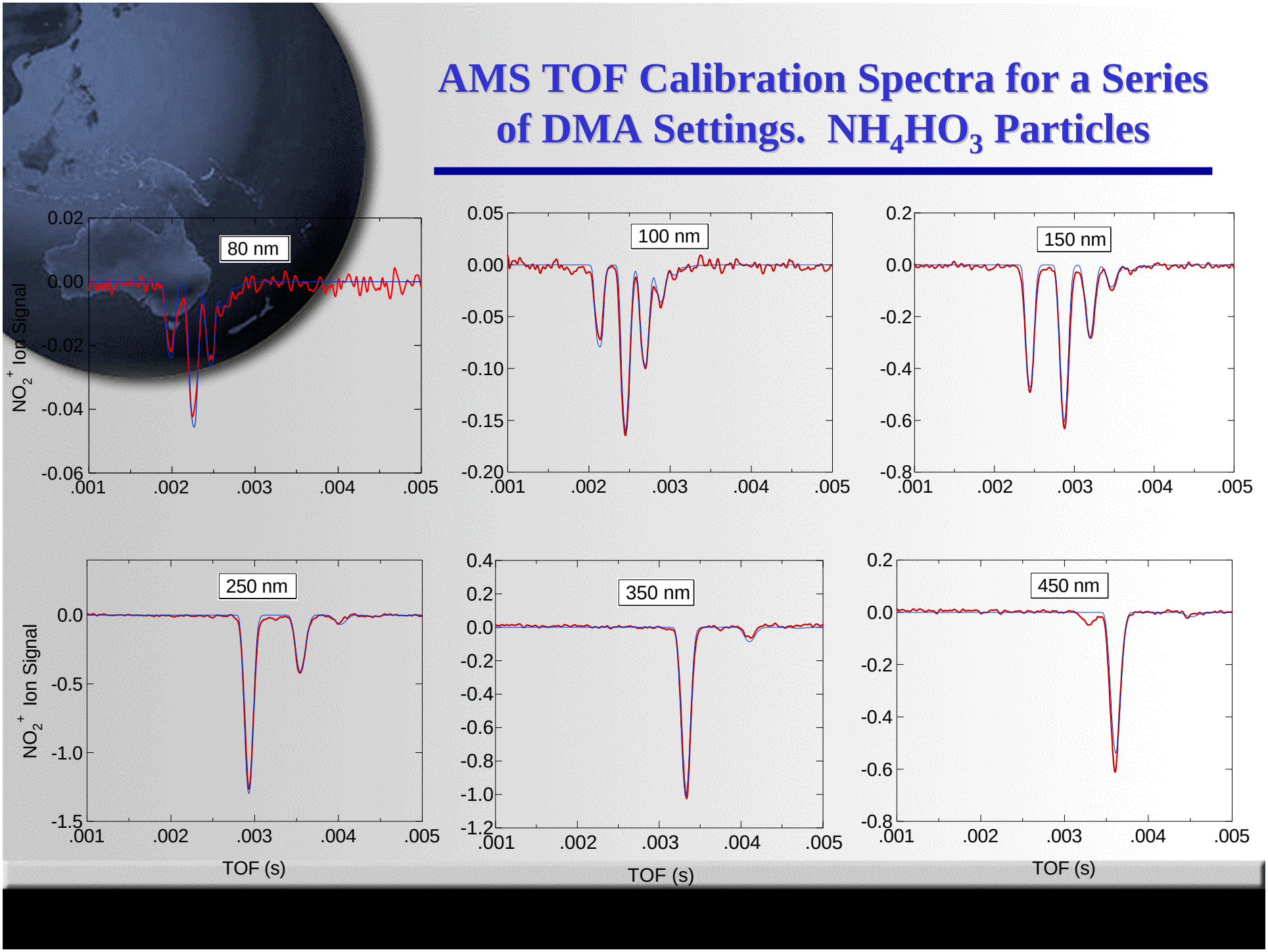
$$vel = \frac{v_g}{1 + (D_{aero} / D_*)^b}$$

$$D_{aero} = D_{geom} * Density * ShapeFactor$$

V_g = 592 m s^{-1}
D^* = 27 .2 (± 0.5) nm
b = 0.479 (± 0.004)



AMS TOF Calibration Spectra for a Series of DMA Settings. NH_4HO_3 Particles

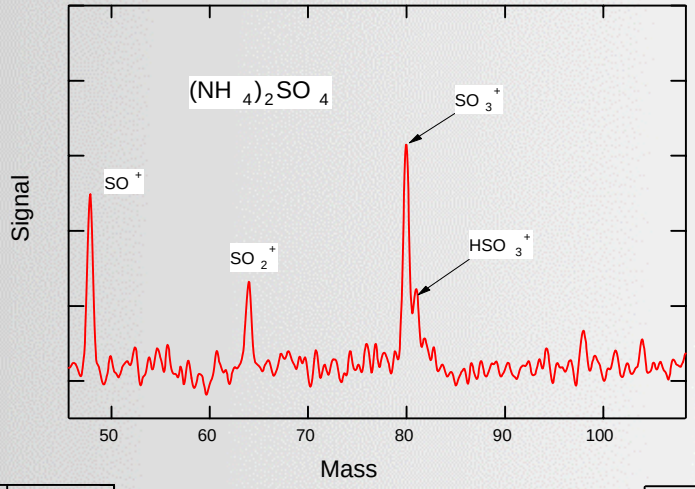


Particle Detection Chamber

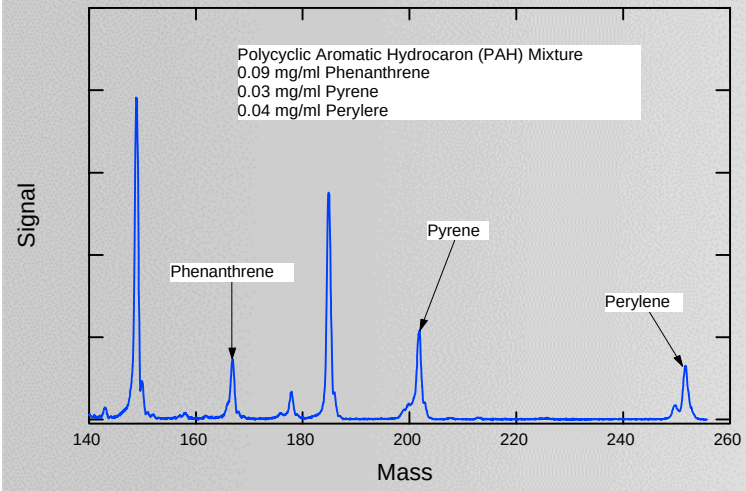
- The particle beam enters the particle detection chamber (PDC) and is focused into a resistively heated closed-end tube where volatile and semi-volatile constituents in or on the particles flash vaporize.
- The vaporization source is coupled to an electron impact ionizer which provides high electron emission current and improved ion focusing and ion extraction.
- The ionizer is coupled to a quadrupole mass spectrometer which can count pulses from individual particles and determine mass and chemical composition.

Sample Mass Spectra of Particulate Matter

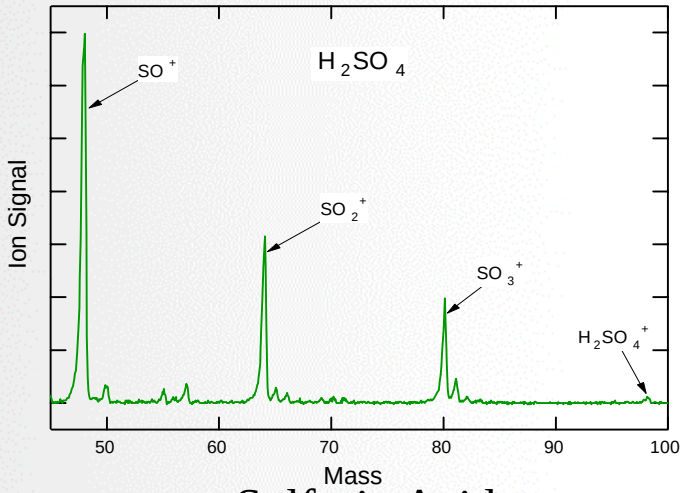
Composition Information by Molecular Mass Spectrometry following Particle Vaporization on a Heated Surface and Electron Impact Ionization



Ammonium Sulfate



Polycyclic Aromatic hydrocarbon Mixture



Sulfuric Acid

Performance Factors

- **Particles must vaporize to be detected.**
  Efficient detection limited to volatile and semi-volatile species.

- **Particles must vaporize efficiently (fast).**
  Influences resolution of aerodynamic size measurement.

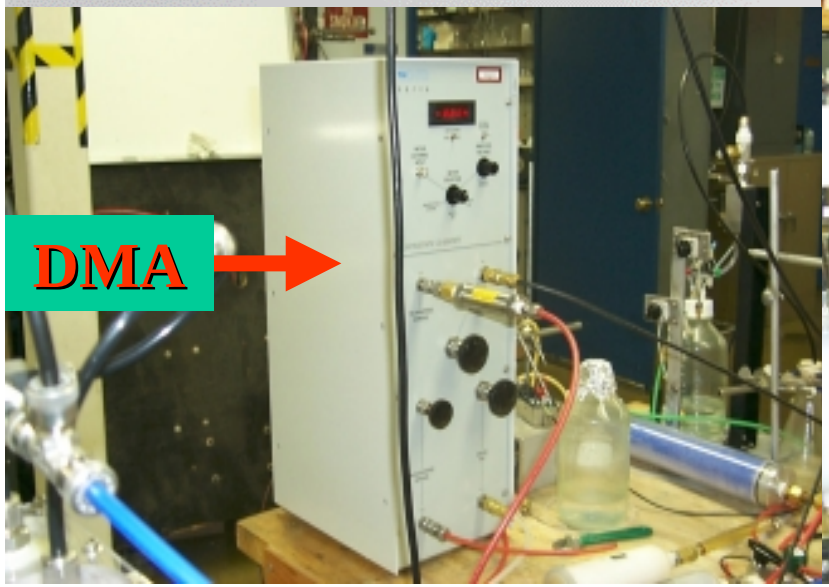
- **Fragmentation of molecular species from the electron impact ionization process.**
  Molecular components can be detected at the same m/z ratio.

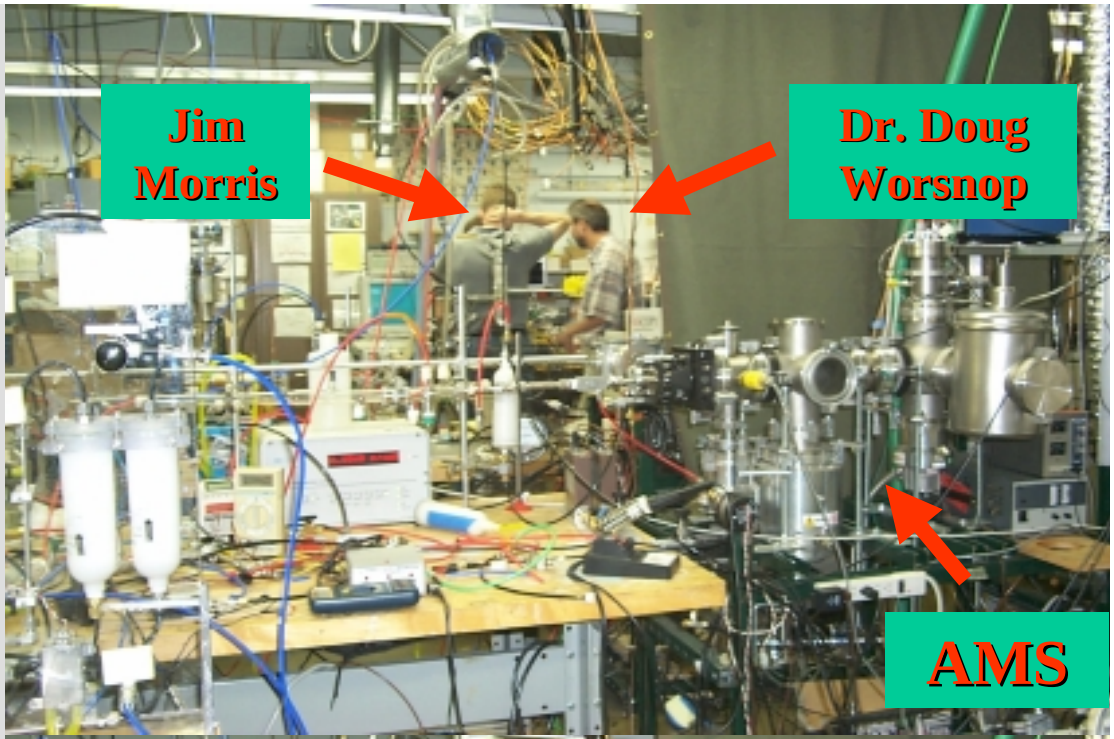
Modeling AMS Performance using DMA

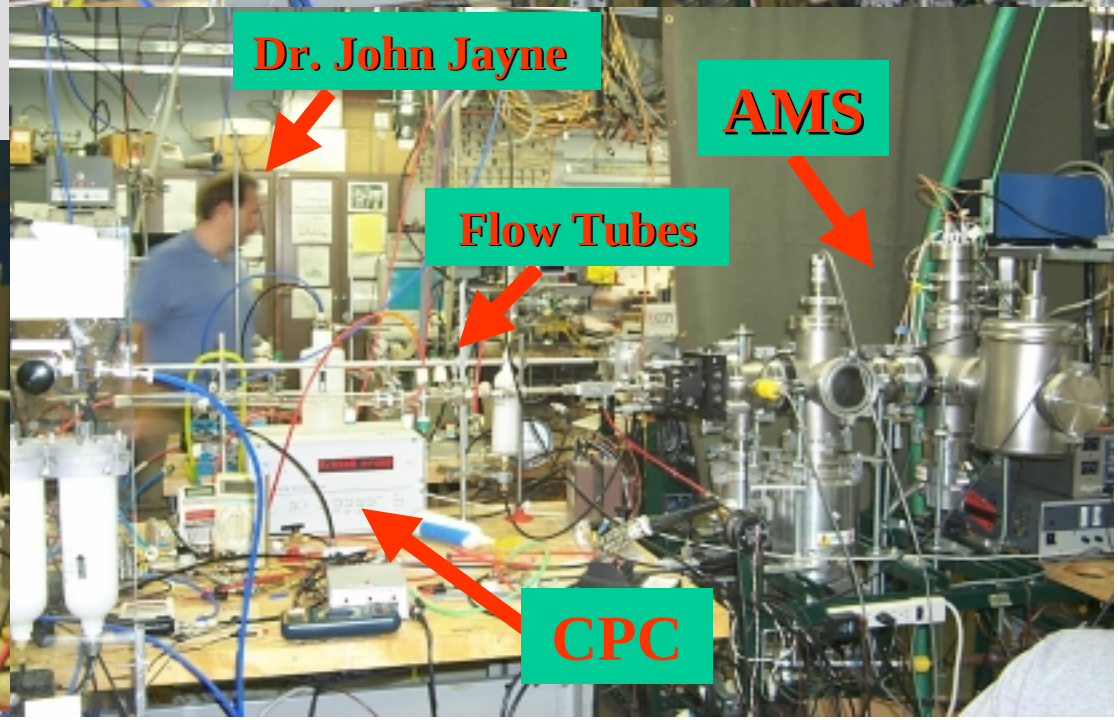
- Produce polydisperse DOP, NH_4NO_3, or oleic acid aerosols with atomizer.
- Select particle size with Differential Mobility Analyzer (DMA) in range where transmission efficiency is < 100 %.
- Sample DMA output concurrently with Condensation Particle Counter (CPC) and AMS.
- Generate number density plot with CPC data and use model to determine time of flight (TOF) for multiple charge diameters.
- Compare model TOF output to AMS output.

Photos of Experimental Setup

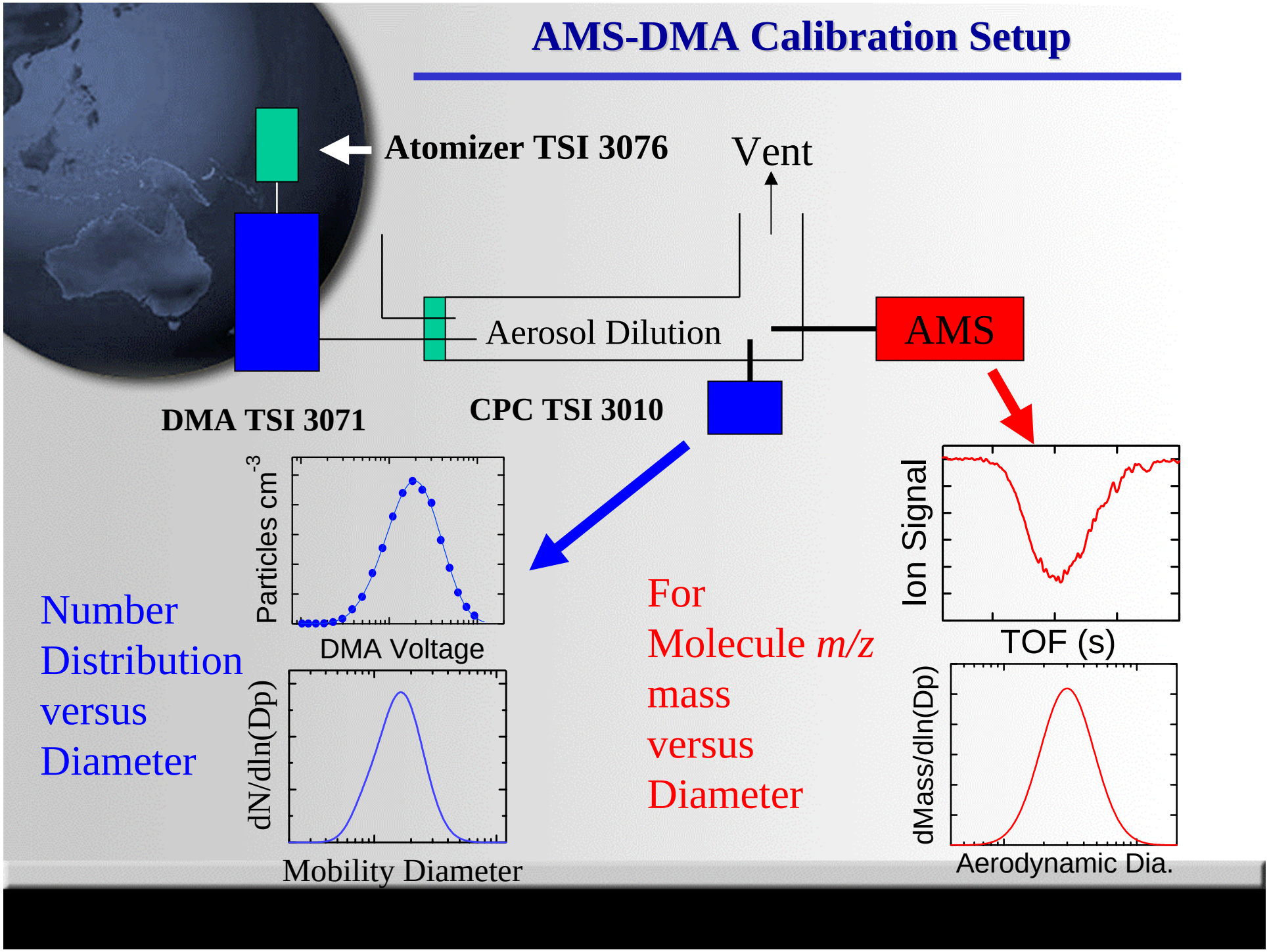
AERODYNE RESEARCH Inc.







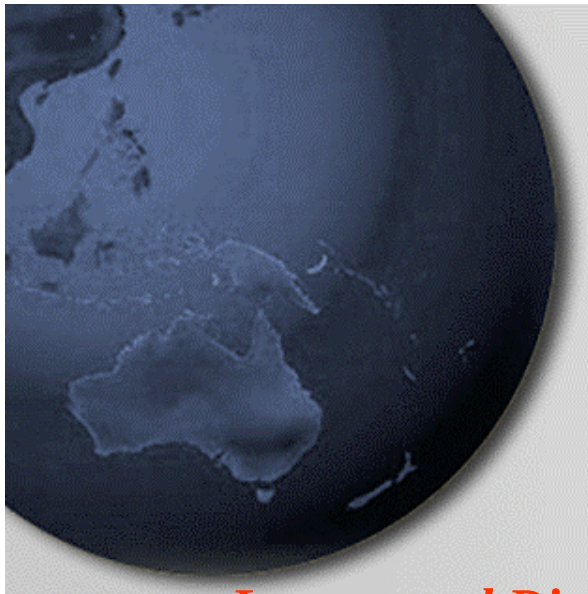
AMS-DMA Calibration Setup

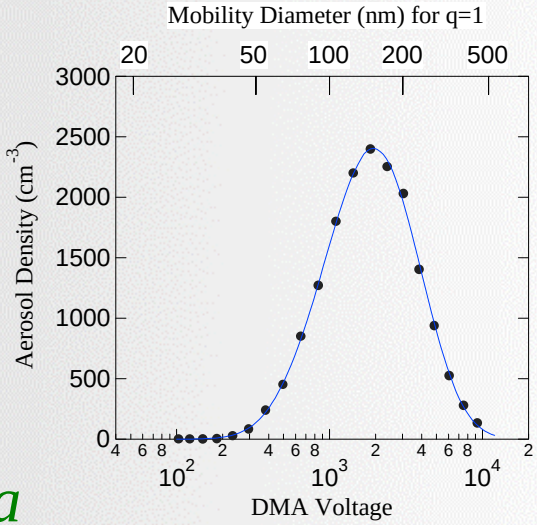


Number Distribution versus Diameter

For Molecule *m/z* mass versus Diameter

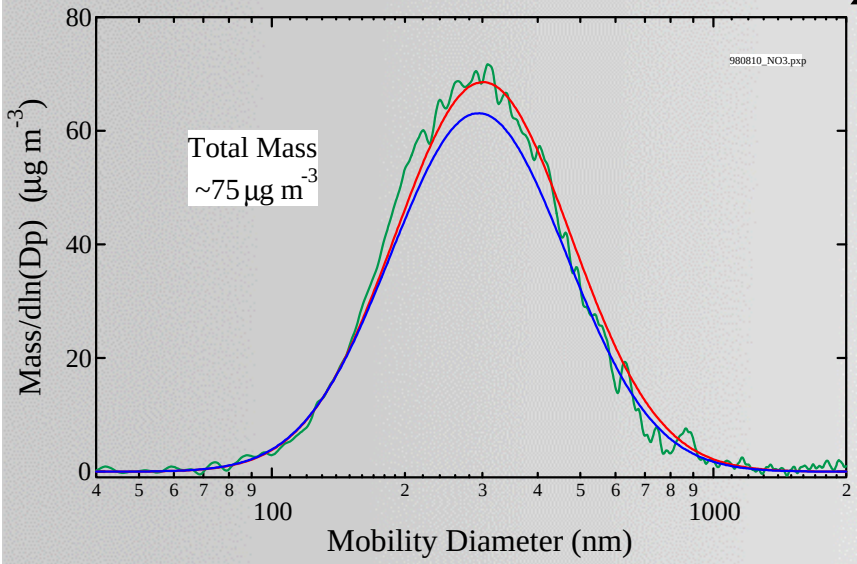
Same Ploydisperse NH_4NO_3 Distribution Measured by AMS and DMA



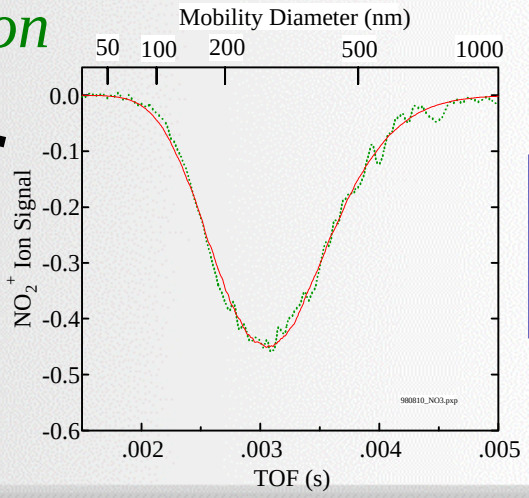


DMA Data:
Number Density Measurement

Log-normal Distribution



Data Inversion



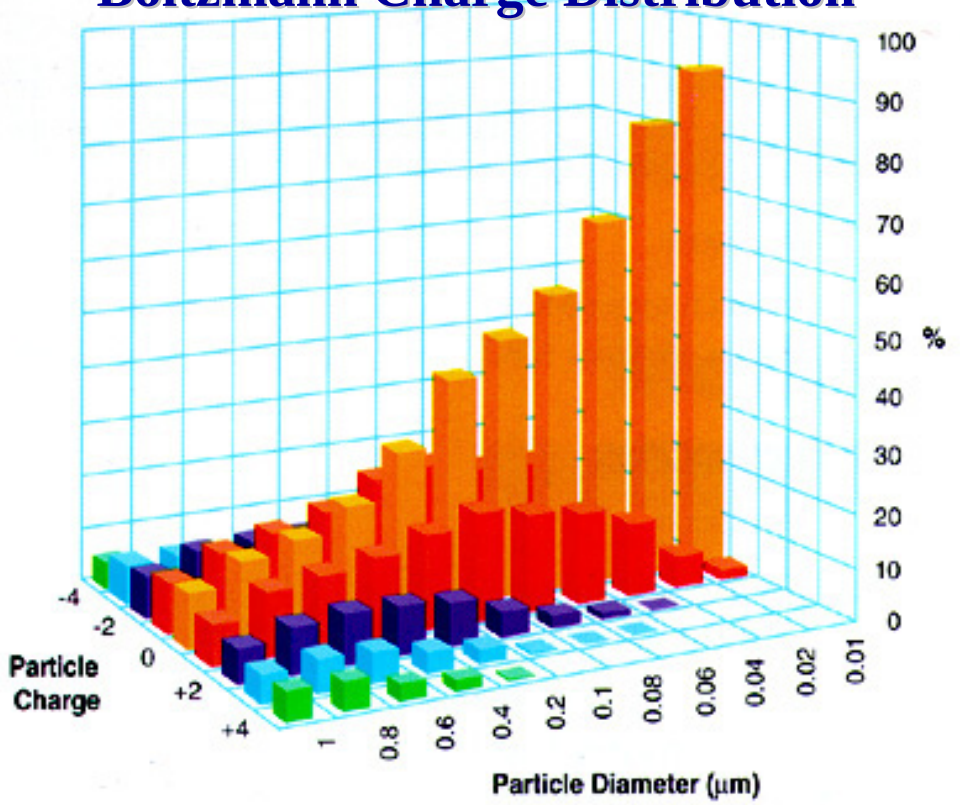
AMS Data:
Mass Measurement

Total Aerosol Mass Measured by AMS and DMA Agree to better than 90%

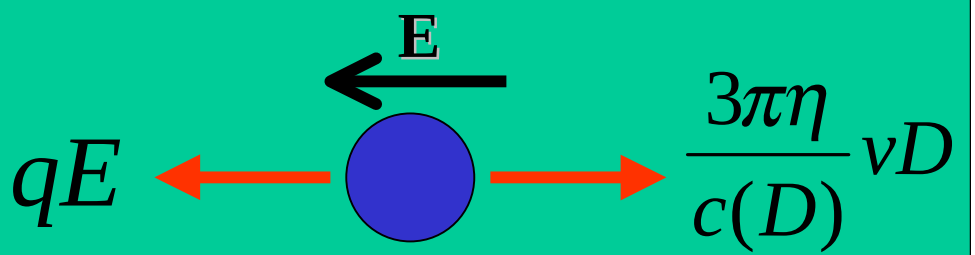
Multiple Charge Diameters

- Aerosols have a Boltzmann charge distribution.
- DMA selects only positive charges:
  - Electric field applied to select desired diameter with charge q = 1.
  - Same electric field also selects diameters of higher charges (q = 1, 2, etc.) with same terminal velocity as desired diameter.

Boltzmann Charge Distribution



Forces on particle in DMA

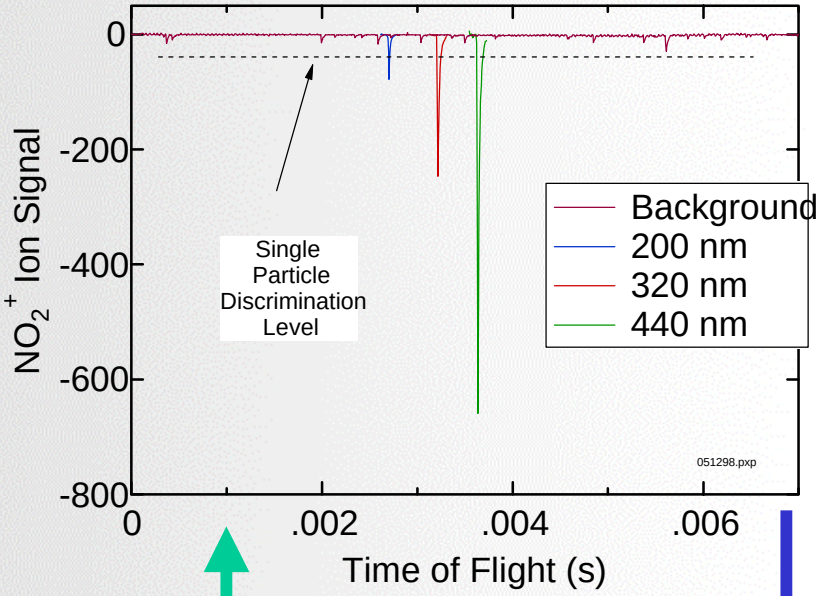


q=charge, D=diameter, v=velocity, c(D)=slip factor, E=electric field, eta=Stoke's const.

Time Resolved Single Particle Detection NH_4NO_3

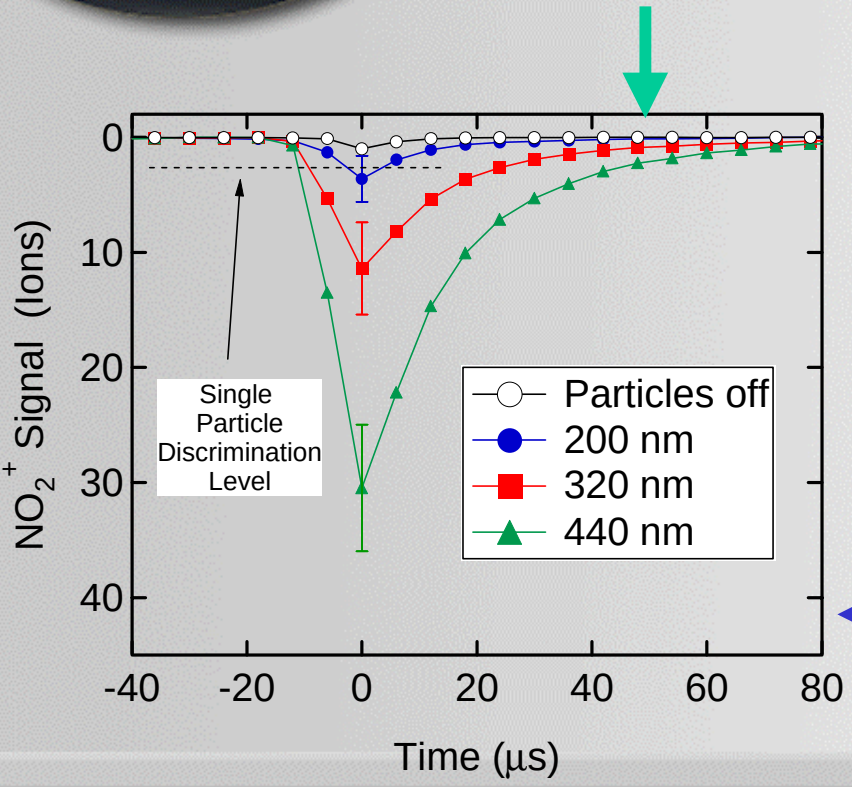
Counting Mode

Single particle detection scales linearly with particle mass



Particle vaporization events are sharply resolved in TOF space.

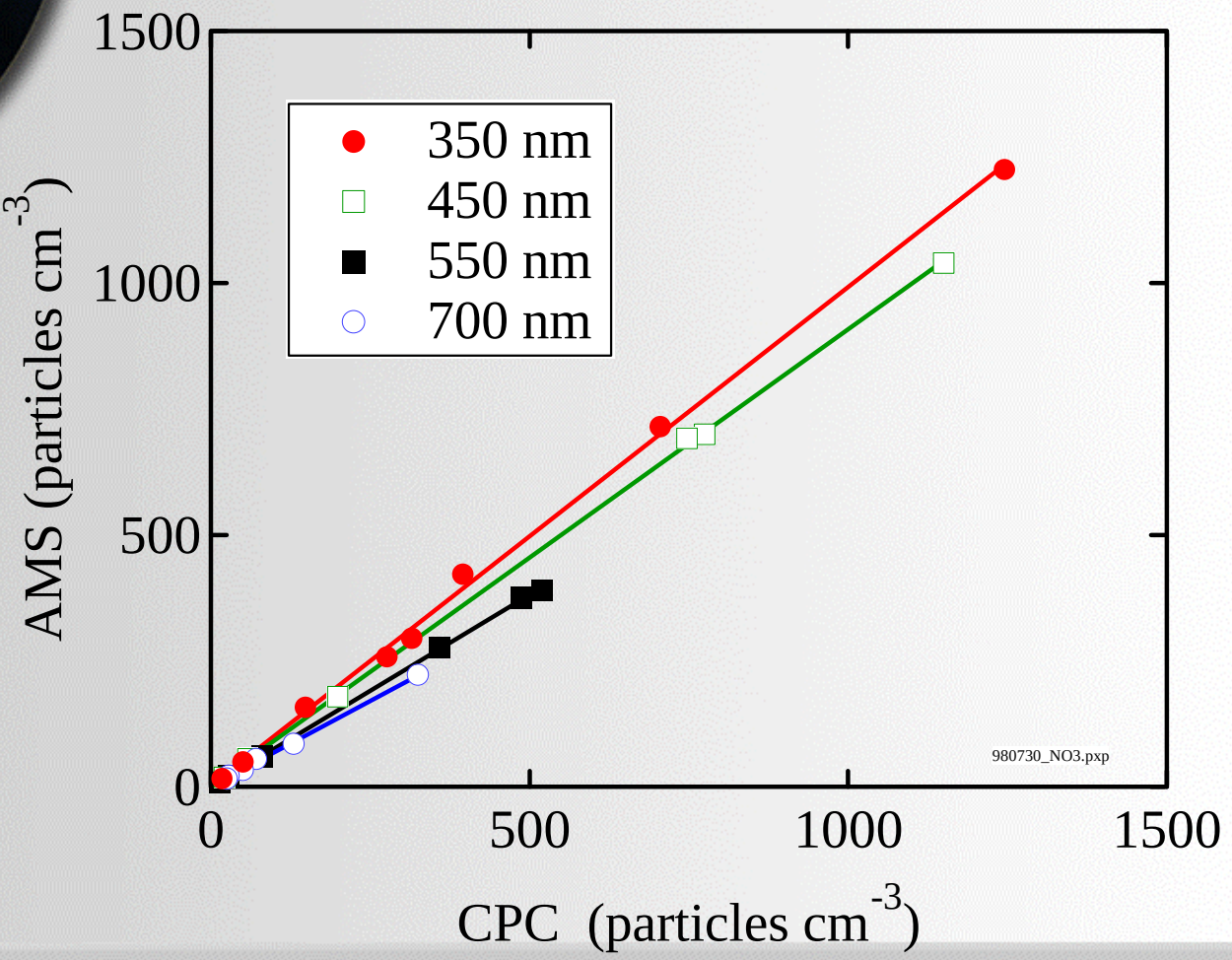
Expanded view of particle data



Measured Collection Efficiency

Compares particle count rate measured by AMS to count rate measured by CPC.

Slope is Collection Efficiency, which is size dependent.



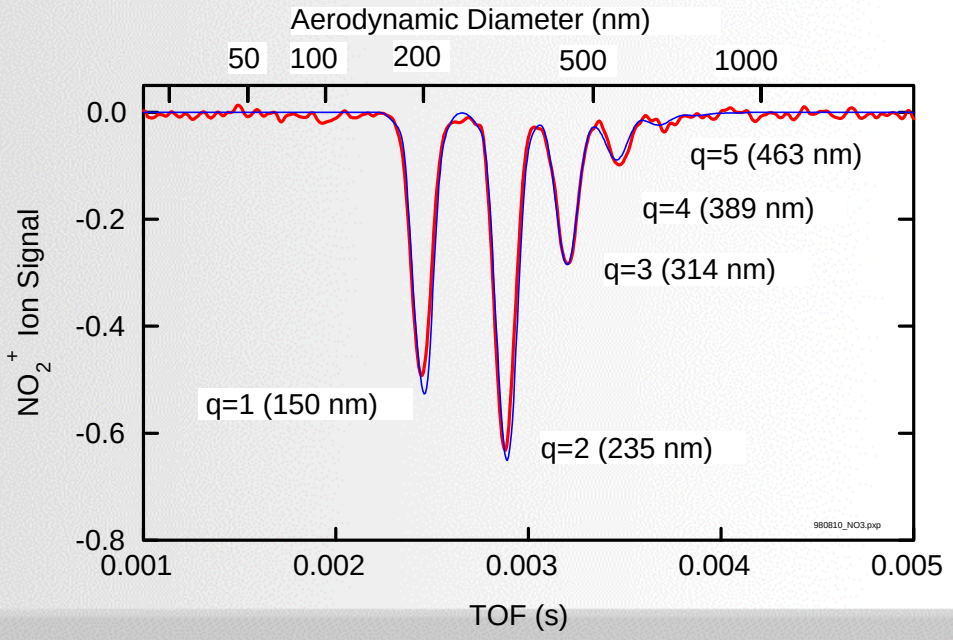
Integration Mode

- Atomize polydisperse aerosols and obtain number density with CPC.
- Select specific diameter of atomized aerosols with DMA and inject into AMS.
- Compare AMS results with model results to determine collection efficiency.

Blue model line accounts for:

1) CPC number distribution parameters.
2) DMA transfer function
3) polydisperse input aerosol Boltzmann distribution
4) a linear mass weighted detection scheme
5) AMS particle collection efficiency
6) AMS transfer function

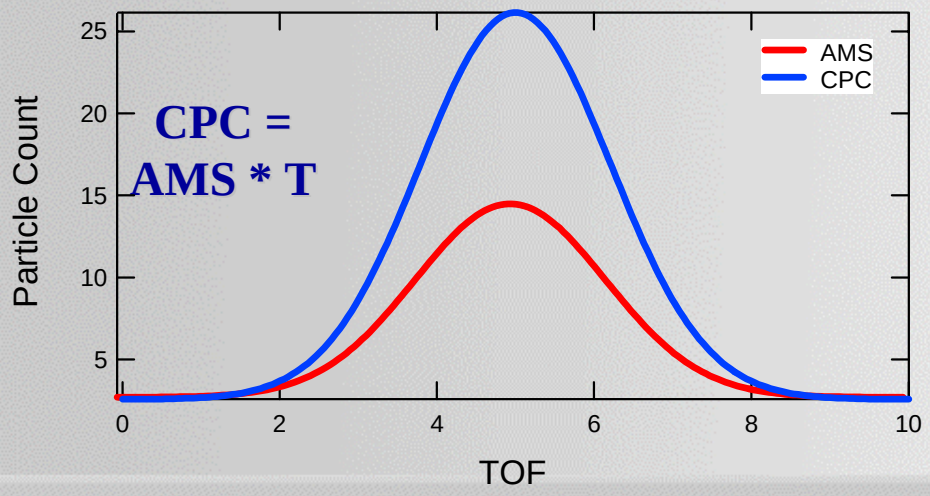
Particle Time-of-Flight (TOF) Spectra for NH_4NO_3 Particles Pre-Sized by the DMA



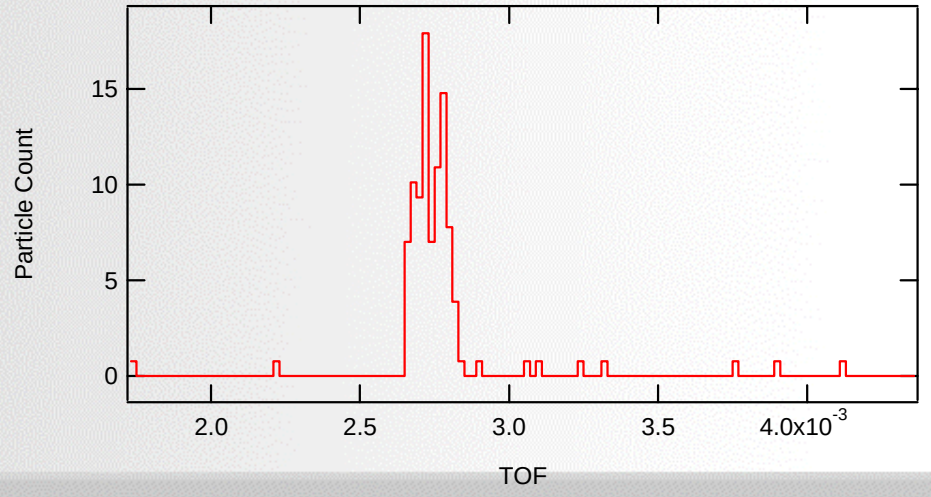
Ideal Experiment

- Atomize polydisperse polystyrene (PSL) spheres of known diameter and inject into CPC and AMS.
- Ideally, the signal in the CPC will be the signal from the AMS times the collection coefficient, T.
- Unfortunately, contamination within the PSL suspension water is counted by the CPC but not the AMS, so T cannot be determined this way for small particles.

Ideal Determination of Transmission

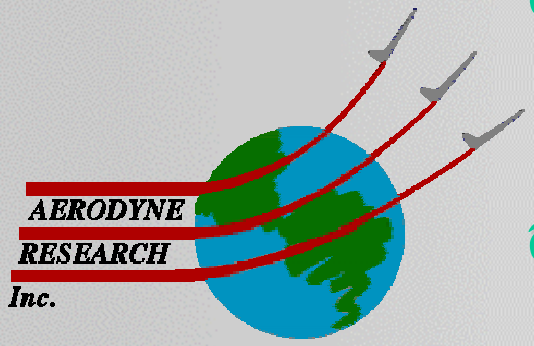


AMS signal for 304 +/- 6 nm PSL spheres



References

- Hinds, William C., Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles. New York: John Wiley & Sons, Inc. 1982.
- Jayne, John T., Leard, Danna C., Zhang, Xuefeng, Davidovits, Paul, Smith, Kenneth A., Kolb, Charles E., Worsnop, Douglas R., *Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles.* Aerosol Science and Technology. 33:49-70, 2000.

Thanks!

- Thanks to Dr. Paul Davidovits at Boston College for setting this job up at Aerodyne.
- Thanks to Dr. John Jayne and Dr. Douglas Worsnop for being great mentors at Aerodyne.
- Thanks to Jim Morris (Ph.D. candidate, Boston College) for letting me hang out with him.
- Thanks to Dr. Gaffney, Milton Constantine, Mary Kinney, and Pat Shoulders for making this summer possible.